United States Patent [19]

Sirrenberg et al.

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[45] **Nov. 16, 1976**

[54] **BENZOYLUREIDO-DIPHENYL ETHER INSECTICIDES**

[75] Inventors: **Wilhelm Sirrenberg,** Sprockhoevel, Westphalia; **Ingeborg Hammann,** Cologne; **wilhelm Stendel,** Wuppertal; **Jürgen Schramm,** Dormagen, all of Germany

[73] Assignee: **Bayer Aktiengesellschaft,** Leverkusen, Germany

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[30] **Foreign Application Priority Data**

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[52] **U.S. Cl.** ..... **424/304;** 260/465 D; 260/553 A; 424/322

[51] **Int. Cl.²** **A01N 9/20;** C07C 121/78; C07C 121/19

[58] **Field of Search** ..... 260/465 D, 553 A; 424/304, 322

[56] **References Cited**

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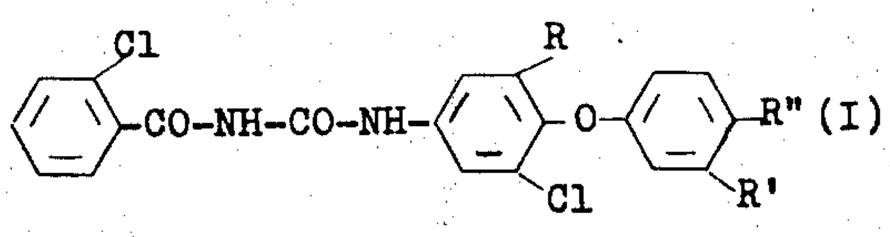
3,798,258 3/1974 Patchett et al. ..... 260/465 X

Primary Examiner—Lewis Gotts
Assistant Examiner—Dolph H. Torrence
Attorney, Agent, or Firm—Burgess, Dinklage & Sprung

[57] **ABSTRACT**

Benzoylureido-diphenyl ethers of the formula



in which

one of R and R′ is hydrogen and the other is chlorine, and

R″ is nitro or cyano,

which possess insecticidal properties.

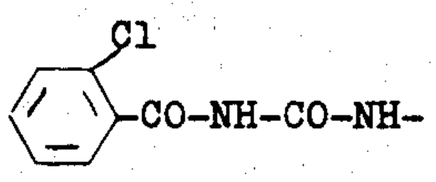
8 Claims, No Drawings

BENZOYLUREIDO-DIPHENYL ETHER INSECTICIDES

The present invention relates to and has for its objects the provision of particular new benzoylureido-diphenyl ethers, i.e. chloro-4'-[N-(N'-(o-chlorobenzoyl))-ureido]-diphenyl ethers, which possess insecticidal properties, active compositions in the form of mixtures of such compounds with solid and liquid dispersible carrier vehicles, and methods for producing such compounds and for using such compounds in a new way especially for combating pests, e.g. insects, with other and further objects becoming apparent from a study of the within specification and accompanying

It is known from German Published Specification DOS 2,123,236 that certain benzoylureas, such as, for example, n-(2,6-dichlorobenzoyl)-N'-(4-chlorophenyl)-(Compound A) and (3,4-dichlorophenyl)-urea (Compound B), possess insecticidal properties.

The present invention provides, as new compounds, the benzoylureido-diphenyl ethers of the general formula



(I),

in which

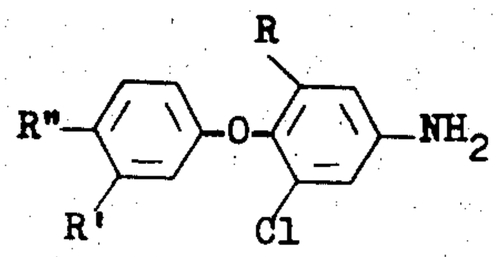
one of R and R' is hydrogen and the other is chlorine, and

R'' is nitro or cyano.

Surprisingly, the benzoylureido-diphenyl ethers according to the invention have a substantially better insecticidal action than the nearest compounds, previously known from the state of the art, which have an analogous structure and the same type of action. The compounds according to the invention thus represent a genuine enrichment of the art.

The present invention also provides a process for the preparation of benzoylurido-diphenyl ether of the formula (I) in which

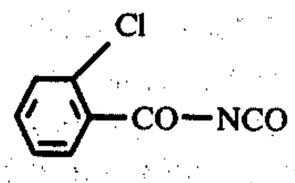
a. a phenoxyaniline of the general formula



(II)

in which

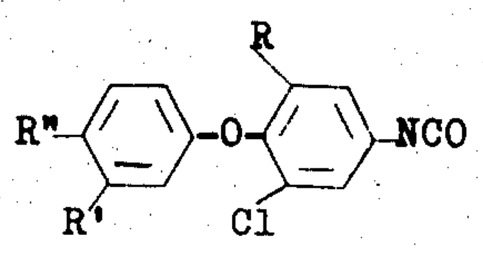
R, R' and R'' have the above-mentioned meanings, is reacted with 2-chlorobenzoylisocyanate of the formula



(III),

if appropriate in the presence of a solvent, or

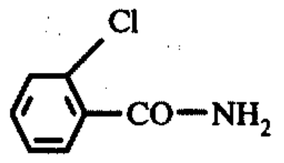
b. a 4-isocyanato-diphenyl ether of the general formula



(IV),

in which

R, R' and R'' have the above-mentioned meanings, is reacted with 2-chlorobenzamide of the formula

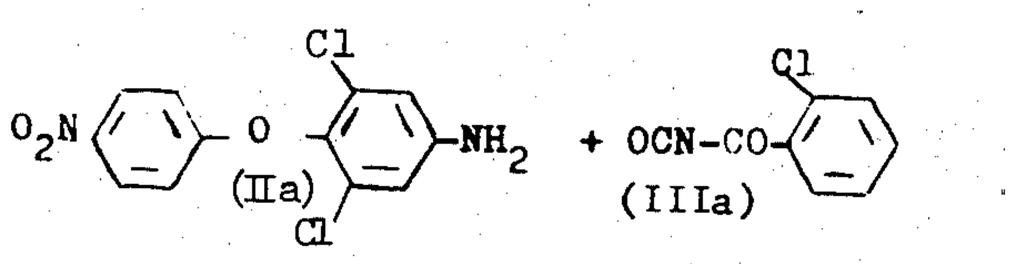


(V),

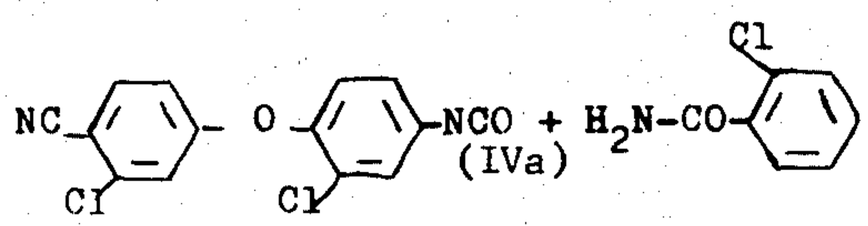
if appropriate in the presence of a solvent.

If, using process variant (a), 3,5-dichloro-4-(4'-nitrophenoxy)-aniline and 2-chlorobenzoylisocyanate are used as the starting materials, and using process variant (b), 3- chloro-4-(3'-chloro-4'-cyano-phenoxy)-phenylisocyanate and 2-chlorobenzamide are used as the starting materials, the courses of the reactions can be represented by the following equations:

(a)



(b)



2-Chlorobenzoylisocyanate (III), to be used as a starting material, is known from the literature and can be prepared according to generally customary pro-

cesses [see A. J. Speziale et al., J. Org, Chem. 30(12), pages 4,306–4,307 (1965)], as can 2-chlorobenzamide (V) (see Beilsteins Handbuch der organischen Chemie (Beilstein's Handbook of Organic Chemistry), volume 9, page 336). The phenoxyanilines (II) can be prepared in accordance with generally customary processes, for example from alkali metal aminophenolates and aromatic nitrohalogeno compounds in a solvent, for example dimethylsulfoxide, and the aminophenoxy-benzonitriles can be prepared likewise (see Jurgen Schramm et al., Justus Liebigs Annalen der Chemie 1970, 740, 169–179). The amino group can be converted into the isocyanate group in accordance with generally customary processes, for example by reaction with phosgene.

The following may be mentioned as examples of the phenoxyanilines (II) and 4-isocyanato-diphenyl ethers (IV) to be used as starting materials: 3-chloro-4-(3′-chloro-4′-nitro- or 3′-chloro-4′-cyanophenoxy)-aniline, 3,5-dichloro-4-(4′-nitro- or 4′-cyanophenoxy)-aniline, as well as 2,6- dichloro-4-isocyanato-4′-nitro-diphenyl ether, 2,6-dichloro-4-isocyanato-4′-cyano-diphenyl ether, 2-chloro-4-isocyanato-3′-chloro-4′-nitro-diphenyl ether and 2-chloro-4-isocyanato-3′-chloro-4′-cyano-diphenyl ether.

The process variants for the preparation of the compounds according to the invention are preferably carried out in the presence of suitable solvents and diluents. Practically all inert organic solvents can be used for this purpose, especially aliphatic and aromatic optionally chlorinated hydrocarbons, such as benzene, toluene, xylene, benzine, methylene chloride, chloroform, carbon tetrachloride and chlorobenzene; ethers, for example diethyl ether, dibutyl ether and dioxane; ketones, for example acetone, methyl ethyl ketone, methyl isopropyl ketone and methyl isobutyl ketone; and nitriles, such as acetonitrile and propionitrile.

The reaction temperature can be varied within a fairly wide range. In general, the reaction is carried out at between 0° to 120° C, preferably at from 70° to 85° C.

In general, the reaction is allowed to take place under normal pressure.

To carry out the process, the reactants are preferably employed in equimolar amounts. An excess of one or other reactant produces no essential advantages.

The 4-isocyanato-diphenyl ethers (IV) to be employed in process variant (b) can be employed as such or, without intermediate isolation, in the form of the reaction mixture obtained from the reaction of amine with phosgene. This reaction mixture in one of the above-mentioned solvents, is treated with 2-chlorobenzamide. The reaction is carried out under the desired conditions and the product which separates out is isolated in the usual manner by filtration, washing and, if appropriate, recrystallization.

The compounds are obtained in a crystalline form of sharp melting point.

As already mentioned, the benzoylureido-diphenyl ethers according to the invention are distinguished by an excellent insecticidal activity. They are not only active against plant pests but also, in the veterinary medicine field, against animal parasites (ectoparasites), such as parasitic fly larvae.

For this reason, the compounds according to the invention can be employed successfully in plant protection against biting and sucking insects, and as pesticides in the veterinary field.

To the sucking insects there belong, in the main, aphids (*Aphididae*) such as the green peach aphid (*Myzus persicae*), the bean aphid (*Doralis fabae*), the bird cherry aphid (*Rhopalosiphum padi*), the pea aphid (*Macrosiphum pisi*) and the potato aphid (*Macrosiphum solanifolii*), the current gall aphid (*Cryptomyzus korschelti*), the rosy apple aphid (*Sappaphis mali*), the mealy plum aphid (*Hyalopterus arundinis*) and the cherry black-fly (*Myzus cerasi*); in addition, scales and mealybugs (*Coccina*), for example the oleander scale (*Aspidiotus hederae*) and the soft scale (*Lecanium hesperidum*) as well as the grape mealybug (*Pseudococcus maritimus*); thrips (*Thysanoptera*), such as *Hercinothrips femoralis*, and bugs, for example the beet bug (*Piesma quadrata*), the red cotton bug (*Dysdercus intermedius*), the bed bug (*Cimex lectularius*), the assassin bug (*Rhodnius prolixus*) and Chagas' bug (*Triatoma infestans*) and, further, cicadas, such as *Euscelis bilobatus* and *Nephotettix bipunctatus*.

In the case of the biting insects, above all there should be mentioned butterfly caterpillars (*Lepidoptera*) such as the diamond-back moth (*Plutella maculipennis*), the gypsy moth (*Lymantria dispar*), the brown-tail moth (*Euproctis chrysorrhoea*) and tent caterpillar (*Malacosoma neustria*); further, the cabbage moth (*Mamestra brassicae*) and the cutworm (*Agrotis segetum*), the large white butterfly (*Pieris brassicae*) the small winter moth (*Cheimatobia brumata*), the green oak tortrix moth (*Tortrix viridana*), the fall armyworm (*Laphygma frugiperda*) and cotton worm (*Prodenia litura*), the ermine moth (*Hyponomeuta padella*), the Mediterranean flour moth (*Ephestia kuhniella*) and the greater wax moth (*Galleria mellonella*).

Also to be classed with the biting insects are beetles (*Coleoptera*), for example the granary weevil (*Sitophilus granarius* = *Calandra granaria*), the Colorado beetle (*Leptinotarsa decemlineata*), the dock beetle (*Gastrophysa viridula*), the mustard beetle (*Phaedon cochleariae*), the blossom beetle (*Meligethes aeneus*), the raspberry beetle (*Byturus tomentosus*), the bean weevil (*Bruchidius* = *Acanthoscelides obtectus*), the leather beetle (*Dermestes frischi*), the khapra beetle (*Trogoderma granarium*), the four beetle (*Tribolium castaneum*), the northern corn billbug (*Calandra* or *Sitophilus zeamais*), the drugstore beetle (*Stegobium paniceum*), the yellow mealworm (*Tenebrio molitor*) and the saw-toothed grain beetle (*Oryzaephilus surinamensis*), and also species living in the soil, for example wireworms (*Agriotes spec.*) and larvae of the cockchafer (*Melolontha melolontha*); cockroaches, such as the German cockroach (*Blattella germanica*), American cockroach (*Periplaneta Americana*), Maderiacockroach (*Leucophaea* or *Rhyparobia maderae*), oriental cockroach (*Blatta orientalis*), the giant cockroach (*Blaberus giganteus*) and the black giant cockroach (*Blaberus fuscus*) as well as *Henschoutedenia flexivitta*; further, *Orthoptera*, for example the house cricket (*Gryllus domesticus*); termites such as the eastern subterranean termite (*Reticulitermes flavipes*) and Hymenoptera such as ants, for example the garden ant (*Lasius niger*).

The Diptera comprise essentially the flies, such as the vinegar fly (*Drosophila melanogaster*), the Mediterranean fruit fly (*Ceratitis capitata*), the house fly (*Musca domestica*), the little house fly (*Fannia canicularis*), the black blow fly (*Phormia regina*) and bluebottle fly (*Calliphora erythrocephala*) as well as the stable fly (*Stomoxys calcitrans*); further, gnats, for example mosqui-

toes such as the yellow fever mosquito (*Aedes aegypti*), the northern house mosquito (*Culex pipiens*) and the malaria mosquito (*Anopheles stephensi*).

The active compounds according to the instant invention can be utilized, if desired, in the form of the usual formulations or compositions with conventional inert (i.e. plant compatible or herbicidally inert) pesticide diluents or extenders, i.e. diluents, carriers or extenders of the type usable in conventional pesticide formulations or compositions, e.g. conventional pesticide dispersible carrier vehicles such as gases, solutions, emulsions, suspensions, emulsifiable concentrates, spray powders, pastes, soluble powders, dusting agents, granules, etc. These are prepared in known manner, for instance by extending the active compounds with conventional pesticide dispersible liquid diluent carriers and/or dispersible solid carriers optionally with the use of carrier vehicle assistants, e.g. conventional pesticide surface-active agents, including emulsifying agents and/or dispersing agents, whereby, for example, in the case where water is used as diluent, organic solvents may be added as auxiliary solvents. The following may be chiefly considered for use as conventional carrier vehicles for this purpose: aerosol propellants which are gaseous at normal temperatures and pressures, such as Freon; inert dispersible liquid diluent carriers, including inert organic solvents, such as aromatic hydrocarbons (e.g. benzene, toluene, xylene, alkyl naphthalenes, etc.), halogenated, especially chlorinated, aromatic hydrocarbons (e.g. chlorobenzenes, etc.), cycloalkanes, (e.g. cyclohexane, etc.), paraffins (e.g. petroleum or mineral oil fractions), chlorinated aliphatic hydrocarbons (e.g. methylene chloride, chloroethylenes, etc.), alcohols (e.g. methanol, ethanol, propanol, butanol, glycol, etc.) as well as ethers and esters thereof (e.g. glycol monomethyl ether, etc.), amines (e.g. ethanolamine, etc.), amides (e.g. dimethyl formamide, etc.), sulfoxides (e.g. dimethyl sulfoxide, etc.), acetonitrile, ketones (e.g. acetone, methyl ethyl ketone, methyl isobutyl ketone, cyclohexanone, etc.), and/or water; as well as inert dispersible finely divided solid carriers, such as ground natural minerals (e.g. kaolins, clays, alumina, silica, chalk, i.e. calcium carbonate, talc, attapulgite, montmorillonite, kieselguhr, etc.) and ground synthetic minerals (e.g. highly dispersed silicic acid, silicates, e.g. alkali silicates, etc.); whereas the following may be chiefly considered for use as conventional carrier vehicle assistants, e.g. surface-active agents, for this purpose: emulsifying agents, such as non-ionic and/or anionic emulsifying agents (e.g. polyethylene oxide esters of fatty acids, polyethylene oxide ethers of fatty alcohols, alkyl sulfates, alkyl sulfonates, aryl sulfonates, albumin hydrolyzates, etc., and especially alkyl arylpolyglycol ethers, magnesium stearate, sodium oleate, etc.); and/or dispersing agents, such as lignin, sulfite waste liquors, methyl cellulose, etc.

Such active compounds may be employed alone or in the form of mixtures with one another and/or with such solid and/or liquid dispersible carrier vehicles and/or with other known compatible active agents, especially plant protection agents, such as other insecticides, or nematocides, acaricides, fungicides, bactericides, rodenticides, herbicides, fertilizers, growth-regulating agents, etc., if desired, or in the form of particular dosage preparations for specific application made therefrom, such as solutions, emulsions, suspensions, powders, pastes, and granules which are thus ready for use.

As concerns commercially marketed preparations, these generally contemplate carrier composition mixtures in which the active compound is present in an amount substantially between about 0.1–95% by weight, and preferably 0.5–90% by weight, of the mixture, whereas carrier composition mixtures suitable for direct application or field application generally contemplate those in which the active compound is present in an amount substantially between about 0.0001–10%, preferably 0.01–1%, by weight of the mixture. Thus, the present invention contemplates overall compositions which comprise mixtures of a conventional dispersible carrier vehicle such as (1) a dispersible inert finely divided carrier solid, and/or (2) a dispersible carrier liquid such as an inert organic solvent and/or water, preferably including a surface-active effective amount of a carrier vehicle assistant, e.g. a surfaceactive agent, such as an emulsifying agent and/or a dispersing agent, and an amount of the active compound which is effective for the purpose in question and which is generally between about 0.0001–95%, and preferably 0.001–95%, by weight of the mixture.

The active compounds can also be used in accordance with the well known ultra-low-volume process with good success, i.e. by applying such compound if normally a liquid, or by applying a liquid composition containing the same, via very effective atomizing equipment, in finely divided form, e.g. average particle diameter of from 50-100 microns, or even less, i.e. mist form, for example by airplane crop spraying techniques. Only up to at most about a few liters/hectare are needed, and often amounts only up to about 15 to 1000 g/hectare, preferably 40 to 600 g/hectare, are sufficient. In this process it is possible to use highly concentrated liquid compositions with said liquid carrier vehicles containing from about 20 to about 95% by weight of the active compound or even the 100% active substance alone, e.g. about 20–100% by weight of the active compound.

Furthermore, the present invention contemplates methods of selectively killing, combating or controlling pests, e.g. insects, which comprises applying to at least one of correspondingly (a) such insects, and (b) the corresponding habitat thereof, i.e. the locus to be protected, e.g. to a growing crop, to an area where a crop is to be grown or to a domestic animal, a correspondingly combative or toxic amount, i.e. an insecticidally effective amount, of the particular active compound of the invention alone or together with a carrier vehicle as noted above. The instant formulations or compositions are applied in the usual manner, for instance by spraying, atomizing, vaporizing, scattering, dusting, watering, squirting, sprinkling, pouring, fumigating, dressing, encrusting, and the like.

It will be realized, of course, that the concentration of the particular active compound utilized in admixture with the carrier vehicle will depend upon the intended application. Therefore, in special cases it is possible to go above or below the aforementioned concentration ranges.

The unexpected superiority and outstanding activity of the particular new compounds of the present invention are illustrated, without limitation, by the following examples:

EXAMPLE 1

Plutella test

Solvent: 3 parts by weight of dimethylformamide
Emulsifier: 1 part by weight of alkylaryl polyglycol ether

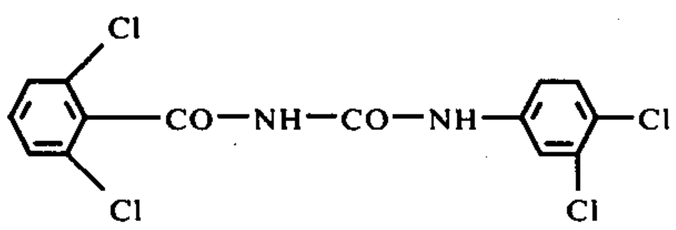
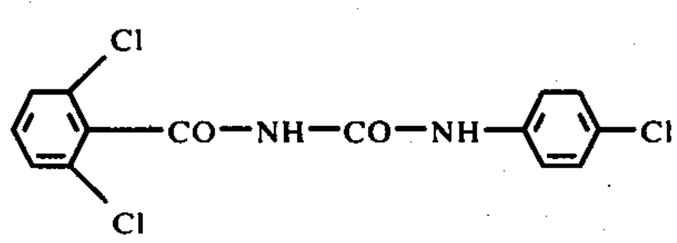
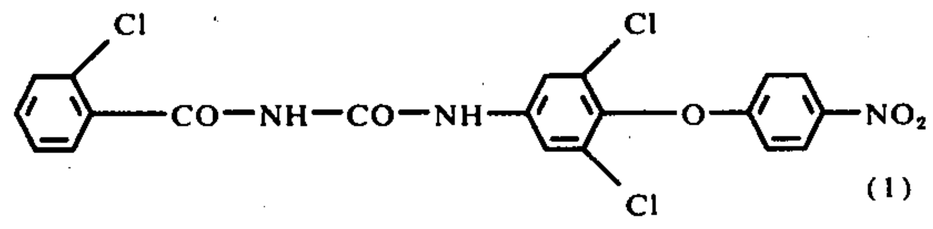
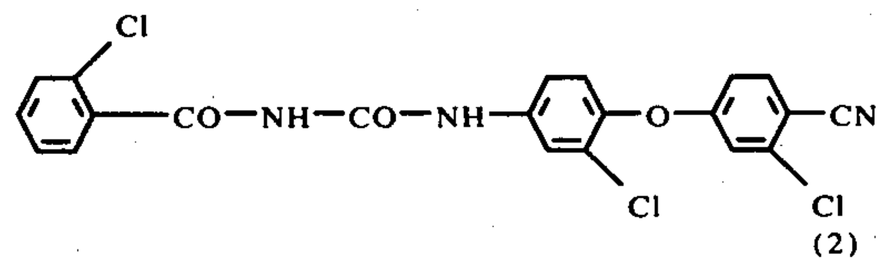
To produce a suitable preparation of active compound, 1 part by weight of the active compound was mixed with the stated amount of solvent containing the stated amount of emulsifier and the concentrate was diluted with water to the desired concentration.

Cabbage leaves (*Brassica oleracea*) were sprayed with the preparation of the active compound until dew moist and were then infested with caterpillars of the diamond-back moth (*Plutella maculipennis*).

After the specified periods of time, the degree of destruction was determined as a percentage: 100% means that all the caterpillars were killed whereas 0% means that none of the caterpillars were killed.

The active compounds, the concentrations of the active compounds, the evaluation times and the results can be seen from the following table:

Table 1

Active compound	*Plutella* test Active compound concentration in %	Degree of destruction in % after 8 days
 (known) (B)	0.1	100
	0.01	100
	0.001	15
 (known) (A)	0.1	65
	0.01	0
 (1)	0.1	100
	0.01	100
	0.001	100
 (2)	0.1	100
	0.01	100
	0.001	100

EXAMPLE 2

Test with parasitic fly larvae

Solvent:	35 parts by weight of ethylene polyglycol monomethyl ether 35 parts by weight of nonylphenol polyglycol ether

To produce a suitable preparation of active compound, 30 parts by weight of the active substance in question were mixed with the stated amount of solvent which contained the above-mentioned proportion of emulsifier and the concentrate thus obtained was diluted with water to the desired concentration.

About 20 fly larvae (*Lucilia cuprina*) were introduced into a test tube which contained approx. 2 cm^3 of horse muscle. 0.5 ml of the preparation of active compound was applied to this horse meat. After 24 hours, the degree of descruction in % was determined. 100% means that all the larvae had been killed and 0% means that no larvae had been killed.

The active compounds investigated, the concentrations of the active compounds used and the results obtained can be seen from the table which follows:

Table 2

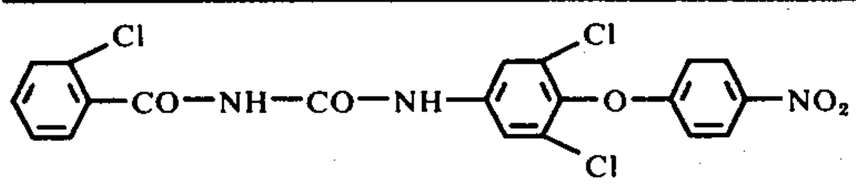
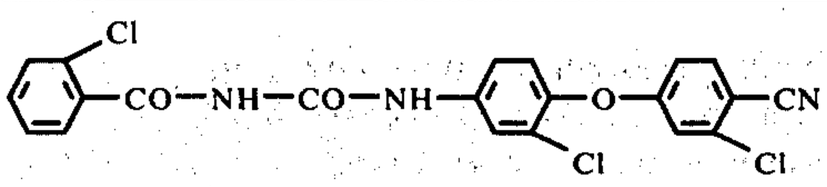
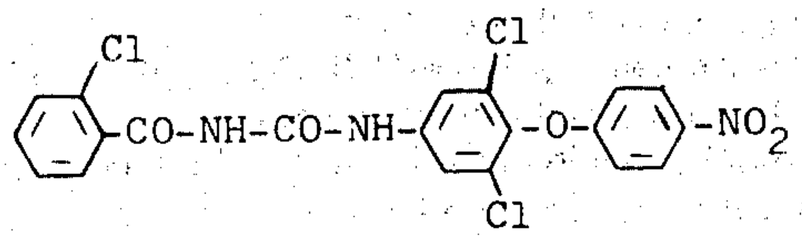
Active compound	Test with parasitic fly larvae/*Lucilia cuprina* res. Active compound concentration in ppm	Degree of destruction in %
 (1)	1,000	100

Table 2-continued

Active compound	Test with parasitic fly larvae/*Lucilia cuprina* res. Active compound concentration in ppm	Degree of destruction in %
 (2)	1,000	100

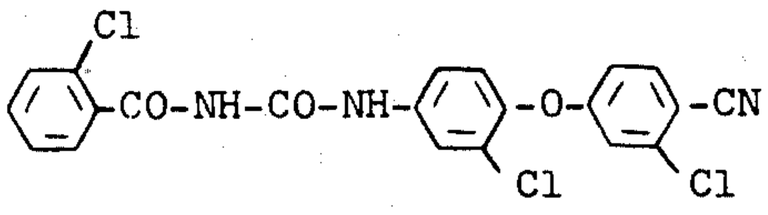
The process of this invention is illustrated by the following preparative Examples.

EXAMPLE 3


(1)

A solution of 5.5 g (0.03 mole) of 2-chlorobenzoylisocyanate in 50 ml of toluene was added dropwise at 80° C to 9 g (0.03 mole) of 3,5-dichloro-4-(4′-nitrophenoxy)-aniline in 150 ml of toluene. The batch was stirred for 1 hour at 80° C and after cooling the product which had precipitated was filtered off and was washed first with toluene and then with petroleum ether. After drying, 10 g (69% of theory) of analytically pure 4-nitro-2′,6′-dichloro-4′-[N-(N′-(o-chlorobenzoyl))-ureido]-diphenyl ether of melting point 184° C were obtained.

EXAMPLE 4


(2)

A solution of 7.3 g (0.04 mole) of 2-chlorobenzoylisocyanate in 50 ml of toluene was added dropwise at 80° C to a solution of 10.2 g (0.04 mole) of 3-chloro-4-(3′-chloro-4′-cyano-phenoxy)-aniline in 100 ml of toluene. The batch was stirred for 1 hour at 80° C and the substance which separated out was filtered off after cooling the reaction mixture to 20° C, and was washed with toluene and petroleum ether. After drying, 12 g (65% of theory) of 3-chloro-4-cyano-2′-chloro-4′-[N-(N′-(o-chlorobenzoyl))-ureido]-diphenyl ether of melting point 209° C were obtained.

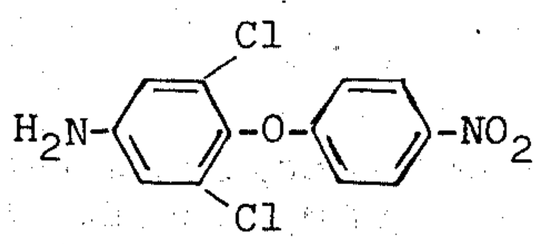
The above compounds could also be obtained from the corresponding 4-isocyanato-diphenyl ethers by reaction with 2-chlorobenzamide.

Other compounds which can be similarly produced in accordance with the invention include:

3-chloro-4-nitro-2′-chloro-4′-[N-(N′(o-chlorobenzoyl))-ureido]-diphenyl ether and

4-cyano-2′,6′-dichloro-4′-[N-(N′-(o-chlorobenzoyl))-ureido]-diphenyl ether.

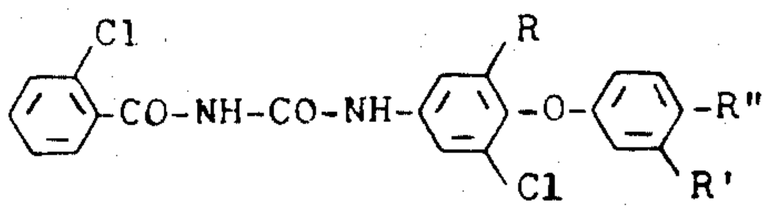
It will be appreciated that the instant specification and examples are set forth by way of illustration and not limitation, and that various modifications and changes may be made without departing from the spirit and scope of the present invention. The process for the production of the starting material according to formula II is illustrated by the following preparation Example:



A solution of 130 g of 86 % potassium hydroxide in 100 ml of water was added to a solution of 384 g (2 mole) of 2,6-dichloro-4-aminophenol in 1,2 l of dimethylsulfoxide. 200 ml of liquid were removed by distillation under reduced pressure. To the residue was added 315 g 4-chloro-1-nitrobenzene. The batch was stirred for 3 hours at 80° C and after cooling the product which had precipitated was filtered of and washed with water. For further purification the precipitate was stirred with a solution of 2 – 3 % sodium hydroxide in water, filtered and washed until neutral with water. After recristallisation from ethanol 291 g (48 %) of a melting point of 130° C were obtained.

What is claimed is:

1. A benzoylureidodiphenyl ether of the formula

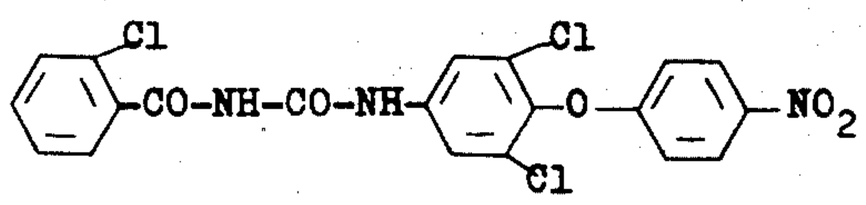


in which

one of R and R′ is hydrogen and the other is chlorine, and

R″ is nitro or cyano.

2. The compound according to claim **1** wherein such compound is 4-nitro-2′,6′-dichloro-4′-[N-(N′-(o-chlorobenzoyl))-ureido]-diphenyl ether of the formula



3. The compound according to claim **1** wherein such compound is 3-chloro-4-cyano-2′-chloro-4′-[N-(N′-(o-chlorobenzoyl))-ureido]-diphenyl ether of the formula

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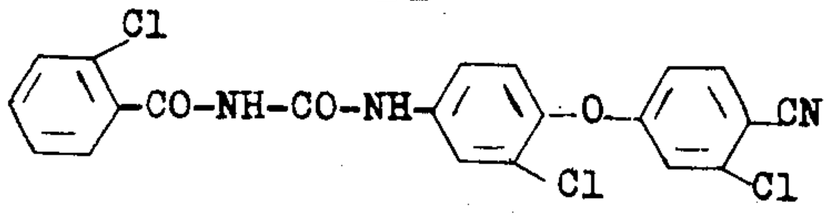
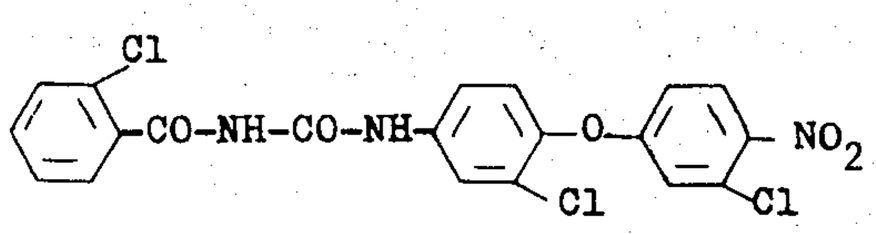


4. The compound according to claim **1** wherein such compound is 3-chloro-4-nitro-2′-chloro-4′-[N-(N′-(o-chlorobenzoyl))-ureido]-diphenyl ether of the formula



5. The compound according to claim **1** wherein such compound is 4-cyano-2′,6′-dichloro-4′-[N-(N′-(o-chlorobenzoyl))-ureido]-diphenyl ether of the formula

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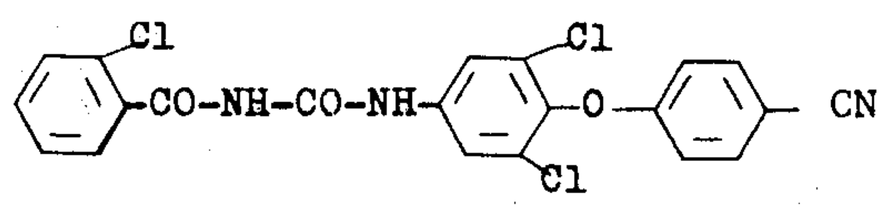

6. An insecticidal composition containing as active ingredient an insecticidally effective amount of a compound according to claim **1** in admixture with a diluent.

7. A method of combating insects which comprises applying to the insects or an insect habitat an insecticidally effective amount of a compound according to claim **1.**

8. The method according to claim **7** in which said compound is

4-nitro-2′,6′-dichloro-4′-[N-(N′-(o-chlorobenzoyl))-ureido]-diphenyl ether,

3-chloro-4-cyano-2′-chloro-4′-[N-(N′-(o-chlorobenzoyl))-ureido]-diphenyl ether,

3-chloro-4-nitro-2′-chloro-4′-[N-(N′-(o-chlorobenzoyl))-ureido]-diphenyl ether, or

4-cyano-2′,6′-dichloro-4′-[N-(N′-(o-chlorobenzoyl))-ureido]-diphenyl ether.

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